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# The Standard Chemical-Thermodynamic Properties of Phosphorus and Some of its Key Compounds and Aqueous Species: An Evaluation of Differences between the Previous Recommendations of NBS/NIST and CODATA

Joseph A. Rard · Thomas J. Wolery

**Abstract** The aqueous chemistry of phosphorus is dominated by P(V), which under typical environmental conditions (and depending on pH and concentration) can be present as the orthophosphate ions  $\text{H}_3\text{PO}_4^0(\text{aq})$ ,  $\text{H}_2\text{PO}_4^-(\text{aq})$ ,  $\text{HPO}_4^{2-}(\text{aq})$ , or  $\text{PO}_4^{3-}(\text{aq})$ . Many divalent, trivalent, and tetravalent metal ions form sparingly soluble orthophosphate phases that, depending on the solution pH and concentrations of phosphate and metal ions, can be solubility limiting phases. Geochemical and chemical engineering modeling of solubilities and speciation requires comprehensive thermodynamic databases that include the standard thermodynamic properties for the aqueous species and solid compounds. The most widely used sources for standard thermodynamic properties are the NBS (now NIST) Tables (from 1982 and earlier; with a 1989 erratum) and the final CODATA evaluation (1989). However, a comparison of the reported enthalpies of formation and Gibbs energies of formation for key phosphate compounds and aqueous species, especially  $\text{H}_2\text{PO}_4^-(\text{aq})$  and  $\text{HPO}_4^{2-}(\text{aq})$ , shows a systematic and nearly constant difference of 6.3 to 6.9  $\text{kJ}\cdot\text{mol}^{-1}$  per phosphorus atom between these two evaluations. The existing literature contains numerous studies (including major data summaries) that are based on one or the other of these evaluations. In this report we examine and identify the origin of this difference and conclude that the CODATA evaluation is more reliable. Values of the standard entropies of the  $\text{H}_2\text{PO}_4^-(\text{aq})$ ,  $\text{HPO}_4^{2-}(\text{aq})$ , and  $\text{PO}_4^{3-}(\text{aq})$  ions at 298.15 K and  $p^\circ = 1$  bar were re-examined in the light of more recent information and data not considered in the CODATA review, and a slightly different value of  $S_m^\circ(\text{H}_2\text{PO}_4^-, \text{aq}, 298.15 \text{ K}) = 90.6 \pm 1.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  was obtained.

**Keywords** Standard entropy · Gibbs energy of formation · Enthalpy of formation · Entropy of formation · Orthophosphates · Phosphorus

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## 1. Introduction

The prediction of solubilities of minerals and other solid phases in water and aqueous electrolyte solutions, and the concentrations and speciation of dissolved ionic and neutral species, is commonly made using geochemical modeling codes such as EQ3/6 [1], FREZCHEM [2], or PHRQPITZ [3]. These modeling codes require a comprehensive thermodynamic database consisting of standard state or reference state thermodynamic properties, and, for aqueous electrolytes, evaluated parameters for a thermodynamic model that is valid over wide ranges of molality and temperature. An example of a very widely used and published thermodynamic database is the one developed at the University of California, San Diego [4] and its extension to low temperatures [5]. A further extension for use with the EQ3/6 modeling code [1] has been described very briefly by Alai *et al.* [6]. These cited databases and modeling codes use representations of the thermodynamic properties of electrolyte solutions to high ionic-strengths based on Pitzer's ion-interaction model [7].

The orthophosphate ion and its hydrolyzed forms generally occur at low levels in natural waters, but they are very important because their presence controls the concentrations of some divalent, trivalent, and tetravalent metal ions owing to the formation of sparingly soluble phases. For example, the commercially important (and nearly insoluble) trivalent rare earth ores xenotime and monazite are mixtures of rare earth orthophosphates [8], with thorium(IV) phosphate also being a constituent of monazite. Phosphorites, consisting mainly of calcium apatite and other calcium orthophosphates are quite common in sedimentary deposits, especially those of

marine origin, and are the major commercial source of phosphorus. Autunite-group minerals such as  $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}(\text{cr})$  have been proposed as solubility-limiting phases for uranium in soils and sediments contaminated with uranium and, along with uranyl silicates, are the solubility limiting phases for secondary minerals produced by the oxidative weathering of natural  $\text{UO}_2(\text{s})$  [9].

Orthophosphate is also a component of many standard pH buffers. The presence of excess amounts of phosphate and polyphosphates, largely from agricultural runoff and treated sewage, gives rise to increased rates of eutrophication in natural waters. Phosphate is an essential component of biological systems, being present for example in bone, DNA, RNA, ADP, and ATP.

In order to model the solubility of sparingly soluble orthophosphate minerals and the speciation of phosphorous in natural waters, a comprehensive thermodynamic database is required for its aqueous species, especially for their standard thermodynamic properties.

Although the aqueous chemistry of phosphorus is dominated by P(V), it is quite complicated. Orthophosphoric acid,  $\text{H}_3\text{PO}_4$ , has three acidic protons and can thus exist as  $\text{H}_3\text{PO}_4^0(\text{aq})$ ,  $\text{H}_2\text{PO}_4^-(\text{aq})$ ,  $\text{HPO}_4^{2-}(\text{aq})$ , or  $\text{PO}_4^{3-}(\text{aq})$  depending on concentration, pH, and temperature. Polymeric phosphate ions are also encountered including the pyrophosphate ion  $\text{P}_2\text{O}_7^{4-}(\text{aq})$  and its hydrolyzed forms, the triphosphate ion  $\text{P}_3\text{O}_{10}^{5-}(\text{aq})$  and its hydrolyzed forms, and higher-order polymers. Aqueous species containing phosphorus in lower valence states are encountered under anaerobic conditions including the orthophosphite ion  $\text{PO}_3^{3-}(\text{aq})$  and its hydrolyzed forms, and the phosphite ion  $\text{PO}_2^{3-}(\text{aq})$  and its hydrolyzed forms; both  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_2$  are

obtained as minor by-products during the combustion of P(cr) by O<sub>2</sub>(g). Because of this multiplicity of aqueous valence states and polymeric and hydrolyzed species, the characterization of the chemical thermodynamic properties of phosphorus is more difficult than for many other elements.

Rossini *et al.* [10] in the National Bureau of Standard's "Circular 500" summarized the results of their previous evaluations of the thermodynamic properties of pure compounds and aqueous species of phosphorus, based on literature coverage to 1949 at "298.16 K". Their evaluated results consisted mainly of the standard enthalpy of formation  $\Delta_f H_m^\circ$  and, in some cases, the standard Gibbs energies of formation  $\Delta_f G_m^\circ$ , the standard molar entropies  $S_m^\circ$ , and the standard molar heat capacities  $C_{p,m}^\circ$ . These tables were subsequently extended and updated by groups of elements in the NBS Technical Note 270 series, *e.g.*, reference [11]. All 8 of the Technical Note 270 series of reports (published between 1965 and 1981) were later combined, with minor corrections, and converted from units of calories to joules [12]. A more recent and widely accepted evaluation of standard values of  $\Delta_f H_m^\circ$  and  $S_m^\circ$  {and of values of  $H^\circ(298.15\text{ K}) - H^\circ(0)$  for pure phases} is the 1989 CODATA evaluation [13]. Grenthe *et al.* [14] have subsequently calculated values of  $\Delta_f G_m^\circ$  and their uncertainties from the CODATA results and gave some additional evaluations.

The CODATA recommended results for phosphorus are limited to P(cr, white), H<sub>2</sub>PO<sub>4</sub><sup>-</sup>(aq), HPO<sub>4</sub><sup>2-</sup>(aq) and several gas phase species. However, assessed values of  $\Delta_f H_m^\circ$  for P<sub>4</sub>O<sub>10</sub>(cr, hexagonal) and PCl<sub>5</sub>(cr) were implied in the CODATA report because they were involved in the thermodynamic cycles used for the evaluations for the properties of the aqueous species, and are based on measurements by Head and

Lewis [15], Schumm *et al.* [16] and Birley and Skinner [17]. All of the evaluations described in this and the preceding paragraph [10–14] are restricted to 298.15 K.

Gurvich *et al.* [18] reported critically assessed thermodynamic properties for various pure compounds (solids, liquids, gases) to high temperatures. The NIST-JANAF tables [19] report thermodynamic properties to very high temperatures, which for phosphorus are restricted to P(cr), P(l), P(g), P<sub>4</sub>O<sub>10</sub>(cr), P<sub>4</sub>O<sub>10</sub>(g), and PCl<sub>5</sub>(g). Barin's [20] values for P<sub>4</sub>O<sub>10</sub>(cr) and P<sub>4</sub>O<sub>10</sub>(g) are essentially identical to the NIST-JANAF values, whereas those of Gurvich *et al.* [18] show some differences and their reported enthalpies of formation of P<sub>4</sub>O<sub>10</sub>(cr), and P<sub>4</sub>O<sub>10</sub>(g) in their tables are given with the wrong sign.

Table 1 summarizes the  $\Delta_f H_m^\circ$ ,  $\Delta_f G_m^\circ$ , and  $S_m^\circ$  values for aqueous PO<sub>4</sub><sup>3-</sup>(aq), HPO<sub>4</sub><sup>2-</sup>(aq), H<sub>2</sub>PO<sub>4</sub><sup>-</sup>(aq), and H<sub>3</sub>PO<sub>4</sub><sup>0</sup>(aq), P(cr, white), P<sub>4</sub>O<sub>10</sub>(cr) and PCl<sub>5</sub>(cr) at 298.15 K from these various evaluations [10–14, 18, 19]. Some differences are expected because the more recent evaluations are based on larger databases that include experimental studies published after the earlier evaluations. In some cases there are large differences, *e.g.*, values of  $\Delta_f H_m^\circ$  vary by 19.7 kJ·mol<sup>-1</sup> for PCl<sub>5</sub>(cr), by 28.5 kJ·mol<sup>-1</sup> for P<sub>4</sub>O<sub>10</sub>(cr), and by 6.3 to 7.0 kJ·mol<sup>-1</sup> for the aqueous ions PO<sub>4</sub><sup>3-</sup>(aq), HPO<sub>4</sub><sup>2-</sup>(aq), and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>(aq). It is worth noting that, except for PCl<sub>5</sub>(cr), the older Circular 500 values of  $\Delta_f H_m^\circ$  and  $\Delta_f G_m^\circ$  [10], and the more recent CODATA values [13] and their extension by the NEA [14, 21], are generally in good agreement, whereas the later NBS values [11,12] are significantly less negative. The value of  $\Delta_f G_m^\circ$  for H<sub>2</sub>PO<sub>4</sub><sup>-</sup>(aq) in the NBS 270 tables [11] is apparently erroneous and was corrected in the later report [12].



The Circular 500 [10] gave a list of references for source papers used for these evaluations but did describe the calculations. In contrast, the NBS 270 series of reports [11] and the combined tables [12] provide no information about the evaluations or source papers for the thermodynamic data. The CODATA evaluations [13] include a list of references and evaluated results for most of the reactions used in the evaluations. However, the CODATA report does not contain a discussion of the origin of differences between their evaluated thermodynamic values and those given in the earlier evaluations [10–12], nor to the best of our knowledge has one been published elsewhere in the open literature.

Because of these significant differences in evaluated thermodynamic values among these published thermodynamic databases for phosphorus, combining values from different databases runs the risk of introducing significant inconsistencies into thermodynamic modeling calculations. The NBS [12] and CODATA evaluations [13] are presently widely used in constructing thermodynamic databases for geochemical and engineering modeling calculations (generally supplemented by values for additional compounds and aqueous species). For example, the CODATA values are an integral part of the thermodynamic assessments for the Nuclear Energy Agency's Thermochemical Data Base project [14, 21] and the extension to radionuclides at Pacific Northwest National Laboratory [22]. Weber *et al.*'s evaluation for orthophosphates [23] is tied to the CODATA values at 298.15 K but is then based on a commercial database at higher temperatures, and they note that the two databases are not consistent in all cases and may require adjustment of some standard thermodynamic values when used in combination. The NBS values were used to fix

some of the 298.15 K standard thermodynamic values for the SUPCRT92 software package [24] (but there are some minor differences mainly resulting from unit conversion and round off in the SUPCRT92 values as exemplified in the slop98.dat data file; see also the paper by Shock and Helgeson [25]). Alberty's [26] database for the Gibbs energy of formation of biochemically-relevant species at 298.15 K is based on the CODATA values for the orthophosphate ions and  $\text{H}_2\text{O}(\text{l})$ , but on the NBS tables for other inorganic and some organic species.

In this report we examine the origin of differences between the NBS/NIST and CODATA evaluations for key compounds and aqueous species of phosphorous that appear in both evaluations. We also re-evaluate the standard entropies of the  $\text{HPO}_4^{2-}(\text{aq})$  and  $\text{H}_2\text{PO}_4^{-}(\text{aq})$  ions based on a more complete coverage of the published literature including some studies published after the CODATA review.

## **2. Examination of the origin of differences between the NBS (1982 and earlier) and the CODATA (1989) evaluations for phosphorus**

Differences among values of evaluated thermodynamic properties can arise from differences in the assessed values of  $\Delta_{\text{f}}H_{\text{m}}^{\circ}$ ,  $\Delta_{\text{f}}G_{\text{m}}^{\circ}$ , or  $S_{\text{m}}^{\circ}$ , or from differences in more than one property. By examining the standard entropies  $S_{\text{m}}^{\circ}$  listed in Table 1 it can be seen that the selected  $S_{\text{m}}^{\circ}$  values from the NBS tables [12] and the CODATA Key Values [13] are the same or nearly so for the listed ions and solid substances, and thus they cannot be the origin of the observed large differences for  $\Delta_{\text{f}}H_{\text{m}}^{\circ}$  and  $\Delta_{\text{f}}G_{\text{m}}^{\circ}$ .

The enthalpies of formation of  $\text{PO}_4^{3-}(\text{aq})$ ,  $\text{HPO}_4^{2-}(\text{aq})$ , and  $\text{H}_2\text{PO}_4^{-}(\text{aq})$  given in the CODATA tables were described [13] as being derived from the enthalpy of formation

of 1 mol  $\text{H}_3\text{PO}_4$  in 100 mol  $\text{H}_2\text{O}$ ,  $\Delta_f H_m^\circ(\text{H}_3\text{PO}_4 \text{ in } 100 \text{ H}_2\text{O}, 298.15 \text{ K}) = -1296.2 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$ , which was stated to be based on the enthalpy of combustion of P(cr) results of Head and Lewis [15] to form  $\text{H}_3\text{PO}_4$  in 40 mol  $\text{H}_2\text{O}$  with appropriate dilution data from 40 to 100 mol of  $\text{H}_2\text{O}$ , along with an independent determination based on the enthalpy of formation of  $\text{PCl}_5(\text{cr})$  of Schumm *et al.* [16] combined with the enthalpy of hydrolysis of Birley and Skinner [17]. However, Birley and Skinner's value of  $\Delta_f H_m^\circ(\text{H}_3\text{PO}_4 \text{ in } 100 \text{ H}_2\text{O}, 298.15 \text{ K}) = -(309.80 \pm 0.35)(4.184) = -1296.2 \pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$  is identical to the CODATA value except for the larger assigned uncertainty. The Head and Lewis combustion result [15], after correction for the enthalpy of dilution from 1 mol  $\text{H}_3\text{PO}_4$  in 40 mol  $\text{H}_2\text{O}$  to 1 mole  $\text{H}_3\text{PO}_4$  in 100 mol  $\text{H}_2\text{O}$  using the NBS values [12], becomes  $\Delta_f H_m^\circ(\text{H}_3\text{PO}_4 \text{ in } 100 \text{ H}_2\text{O}, 298.15 \text{ K}) = -(1294.3 \pm 1.6) - 0.6 = -1294.9 \pm 1.6 \text{ kJ}\cdot\text{mol}^{-1}$ . These calculations imply that the CODATA value of  $\Delta_f H_m^\circ(\text{H}_3\text{PO}_4 \text{ in } 100 \text{ H}_2\text{O}, 298.15 \text{ K}) = -1296.2 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$  was actually obtained solely from the  $\text{PCl}_5(\text{cr})$  data, unless there are some additional small but undescribed corrections to the data based on combustion of P(cr) that somehow bring it into exact agreement with this value (which is improbable). The CODATA choice of  $\Delta_f H_m^\circ(\text{H}_3\text{PO}_4 \text{ in } 100 \text{ H}_2\text{O}, 298.15 \text{ K})$  corresponds to  $\Delta_f H_m^\circ(\text{P}_4\text{O}_{10}, \text{cr}, 298.15 \text{ K}) = -3008.2 \text{ kJ}\cdot\text{mol}^{-1}$ , which is essentially identical to  $\Delta_f H_m^\circ(\text{P}_4\text{O}_{10}, \text{cr}, 298.15 \text{ K}) = -3008.3 \pm 5.2 \text{ kJ}\cdot\text{mol}^{-1}$  recommended by Schumm *et al.* [16]. This value agrees well with the assessed value of  $\Delta_f H_m^\circ(\text{P}_4\text{O}_{10}, \text{cr}, 298.15 \text{ K}) = -3010.1 \pm 3.2 \text{ kJ}\cdot\text{mol}^{-1}$  from Gurvich *et al.* [18], which is based on essentially the same source data, and  $\Delta_f H_m^\circ(\text{P}_4\text{O}_{10}, \text{cr}, 298.15 \text{ K}) = -3009.9 \text{ kJ}\cdot\text{mol}^{-1}$  given in the

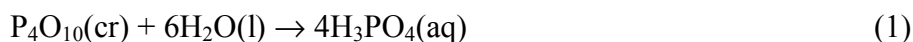
NIST-JANAF tables [19] that is based on the enthalpy of combustion results reported by Egan and Luff [27].

Values of  $\Delta_f G_m^\circ$  for  $\text{PO}_4^{3-}(\text{aq})$ ,  $\text{HPO}_4^{2-}(\text{aq})$ ,  $\text{H}_2\text{PO}_4^-(\text{aq})$ , and  $\text{H}_3\text{PO}_4^0(\text{aq})$  from NBS tables [12] and those calculated in the NEA reviews [14, 21] from information from the CODATA report [13] and additional evaluations are given in Table 1, and differ by  $\Delta(\Delta_f G_m^\circ) = 6.83 \pm 0.06 \text{ kJ}\cdot\text{mol}^{-1}$  where the uncertainty is the 95% confidence limit. This nearly constant difference between the  $\Delta_f G_m^\circ$  values implies that the dissociation constants of orthophosphoric acid used in the NBS evaluation are identical or nearly so to those described in the CODATA evaluation. If a similar examination is made of the  $\Delta_f H_m^\circ$  values summarized in Table 1, there is a systematic trend from  $\Delta(\Delta_f H_m^\circ) = 7.0 \text{ kJ}\cdot\text{mol}^{-1}$  for  $\text{PO}_4^{3-}(\text{aq})$ ,  $\Delta(\Delta_f H_m^\circ) = 6.9 \text{ kJ}\cdot\text{mol}^{-1}$  for  $\text{HPO}_4^{2-}(\text{aq})$ ,  $\Delta(\Delta_f H_m^\circ) = 6.3 \text{ kJ}\cdot\text{mol}^{-1}$  for  $\text{H}_2\text{PO}_4^-(\text{aq})$ , to  $\Delta(\Delta_f H_m^\circ) = 5.8 \text{ kJ}\cdot\text{mol}^{-1}$  for  $\text{H}_3\text{PO}_4^0(\text{aq})$ . The average difference is  $\Delta(\Delta_f H_m^\circ) = 6.5 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$ , where the uncertainty is the 95% confidence limit, which agrees with the  $\Delta(\Delta_f G_m^\circ)$  value within these uncertainty limits. However, these variations for  $\Delta(\Delta_f H_m^\circ)$  may imply that the enthalpies of dissociation of the acidic protons of  $\text{H}_3\text{PO}_4(\text{aq})$  used in the NBS evaluations (which are not known to us) are different from those used in the CODATA evaluations that are described in reference [13].

Because the  $\Delta_f H_m^\circ$  values for  $\text{PO}_4^{3-}(\text{aq})$ ,  $\text{HPO}_4^{2-}(\text{aq})$ ,  $\text{H}_2\text{PO}_4^-(\text{aq})$ , and  $\text{H}_3\text{PO}_4^0(\text{aq})$  in the CODATA and NEA evaluations [13, 14] were based on thermodynamic cycles that include  $\text{P}_4\text{O}_{10}(\text{cr})$  and  $\text{PCl}_5(\text{cr})$ , it is reasonable to expect that similar thermodynamic cycles were used in the NBS evaluations [11, 12]. However, the

values of  $\Delta_f H_m^\circ(\text{PCl}_5, \text{cr}, 298.15 \text{ K})$  from the two evaluations are very close as shown in Table 1, and therefore thermodynamic calculations involving this compound could only account for a very small fraction of the observed differences for the enthalpies of formation of the aqueous species. It is more likely that the observed differences are the result of differences between different sources for the enthalpies of combustion of  $\text{P}(\text{cr})$  to yield  $\text{H}_3\text{PO}_4(\text{aq})$  that are reflected in the values of  $\Delta_f H_m^\circ(\text{P}_4\text{O}_{10}, \text{cr}, 298.15 \text{ K})$ .

Dissolution of  $\text{P}_4\text{O}_{10}(\text{cr})$  in water yields aqueous solutions of orthophosphoric acid by the reaction:



From the results summarized in Table 1 for the NBS [12] and CODATA-based [13, 14] evaluations, the difference in  $\Delta_f H_m^\circ(\text{P}_4\text{O}_{10}, \text{cr}, 298.15 \text{ K})$  values yield  $\Delta(\Delta_f H_m^\circ)/4 = 24.2/4 = 6.1 \text{ kJ}\cdot\text{mol}^{-1}$ , which is within the uncertainty limits of the value  $\Delta(\Delta_f H_m^\circ) = 6.5 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$  derived two paragraphs above for the aqueous species. The fairly consistent systematic differences observed for  $\Delta(\Delta_f H_m^\circ)$  and  $\Delta(\Delta_f G_m^\circ)$  between these two evaluations clearly resulted from the use of inconsistent values for the enthalpy of combustion of  $\text{P}(\text{cr})$  in the two evaluations.

An examination of all of the source papers cited in the CODATA evaluation [13] identified only one that reported the value  $\Delta_f H_m^\circ(\text{P}_4\text{O}_{10}, \text{cr}, 298.15 \text{ K}) = -2984.0 \text{ kJ}\cdot\text{mol}^{-1}$  that is identical to the value given in the NBS tables [11, 12]. This value, taken from the study of Holmes [28], was not used in the CODATA evaluation. Although the calculations and references are not given in the NBS evaluations, Dr. Donald G. Archer of NIST/Gaithersburg [29] was able to locate information that

confirms that the paper of Holmes was the source of the NBS value for  $\Delta_f H_m^\circ(\text{P}_4\text{O}_{10}, \text{cr}, 298.15 \text{ K})$ . As discussed by Head and Lewis [15] and Irving and McKerrell [30], that result reported by Holmes now appears to be discredited. Head and Lewis [15] re-determined the enthalpy of combustion of  $\text{P}(\text{cr})$  and Irving and McKerrell [30] combined their enthalpy of solution of  $\text{P}_4\text{O}_{10}(\text{cr})$  with the enthalpy of combustion results of Egan and Luff [27]; their consistent results also agree well with that obtained from the enthalpies of formation and hydrolysis of  $\text{PCl}_5(\text{cr})$  [16,17].

The examination given here implies that the evaluated values of standard thermodynamic properties for  $\text{PO}_4^{3-}(\text{aq})$ ,  $\text{HPO}_4^{2-}(\text{aq})$ ,  $\text{H}_2\text{PO}_4^-(\text{aq})$ , and  $\text{H}_3\text{PO}_4^0(\text{aq})$  in the NBS evaluations [11,12] are probably systematically in error because of the use of a questionable enthalpy of combustion enthalpy datum [28] in their evaluation; consequently, the corresponding CODATA values [13] are probably more reliable.

A complete re-evaluation of the standard thermodynamic properties of all of the aqueous orthophosphate species and phosphorus compounds evaluated in the CODATA effort [13] is beyond the scope of the present report. We are not aware of any studies that would yield a significant improvement in the values of  $\Delta_f H_m^\circ(\text{P}_4\text{O}_{10}, \text{cr}, 298.15 \text{ K})$  or  $\Delta_f H_m^\circ(\text{PCl}_5, \text{cr}, 298.15 \text{ K})$  that are needed for the evaluation of the enthalpies of formation of the aqueous orthophosphate species. Thus, at this time, we recommend that the evaluated enthalpies of formation reported in the CODATA evaluation be retained.

### **3. Examination and extension of the CODATA evaluation of the standard entropies of the $\text{HPO}_4^{2-}(\text{aq})$ and $\text{H}_2\text{PO}_4^-(\text{aq})$ ions**

The evaluation of the thermodynamic properties for the orthophosphate ion and its protonated species for the CODATA tables [13] is complicated and utilizes thermodynamic cycles involving a number of compounds of phosphorus. It was pointed out above that the enthalpies of formation of the aqueous species are based on calorimetric data for  $\text{P}_4\text{O}_{10}(\text{cr})$  and  $\text{PCl}_5(\text{cr})$ , the dissolution of  $\text{P}_4\text{O}_{10}(\text{cr})$  into water, the hydrolysis of  $\text{PCl}_5(\text{cr})$ , *etc.* Relating the thermodynamic properties of  $\text{PO}_4^{3-}(\text{aq})$ ,  $\text{HPO}_4^{2-}(\text{aq})$ , and  $\text{H}_2\text{PO}_4^{-}(\text{aq})$  involves the enthalpies of ionization of the various acidic ions and the dissociation constants of these acids.

In the CODATA evaluation [13] the standard entropies of the aqueous species  $\text{HPO}_4^{2-}(\text{aq})$  and  $\text{H}_2\text{PO}_4^{-}(\text{aq})$  are derived from the entropies of the solid compounds  $\text{KH}_2\text{PO}_4(\text{cr})$ ,  $(\text{NH}_4)\text{H}_2\text{PO}_4(\text{cr})$  and  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$ , together with their entropies of solution into water. Because the entropies of solution are not directly measurable, they are based on the standard enthalpies and Gibbs energies of solution, and the Gibbs energies of solution in turn are based on solubilities and activity coefficients (and in some cases the activity of water) of the saturated solutions.

The standard entropy of  $\text{KH}_2\text{PO}_4(\text{cr})$  is based on the heat capacity measurements of Stephenson and Hooley [31] from 16.1 to 299.1 K, who reported  $S_m^\circ(\text{KH}_2\text{PO}_4, \text{cr}, \text{“298.19 K”}) = (32.23 \pm 0.1)(4.184) = (134.85 \pm 0.42) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ . The value  $S_m^\circ(\text{KH}_2\text{PO}_4, \text{cr}, 298.15 \text{ K}) = (134.85 \pm 0.45) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  accepted in the CODATA report [13] is identical, except for the slightly larger uncertainty and it was apparently not corrected for the small changes in the temperature scale. Note that “298.19 K” is equivalent to the modern 298.15 K. Kogan and Chernyaev [32] reported heat

capacities of  $\text{KH}_2\text{PO}_4(\text{cr})$  from approximately 60 to 300 K, and used the lower temperatures heat capacities of Stephenson and Hooley to evaluate their standard entropy. The standard entropy reported by Kogan and Chernyaev,  $S_m^\circ(\text{KH}_2\text{PO}_4, \text{cr}, 298.15 \text{ K}) = (32.00 \pm 0.30)(4.184) = (133.9 \pm 1.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , was not cited in the CODATA report. However, this value agrees with the Stephenson and Hooley / CODATA value within these uncertainty limits. The complete Kogan and Chernyaev report is a deposited document that we have not obtained. We concur with the CODATA choice of the more precise value from Stephenson and Hooley [31].

Stephenson and Zettlemoyer [33] reported heat capacities of  $(\text{NH}_4)_2\text{HPO}_4(\text{cr})$  from 18.1 to 299.3 K and reported a standard entropy of  $S_m^\circ\{(\text{NH}_4)_2\text{HPO}_4, \text{cr}, "298.19 \text{ K}"\} = (36.32 \pm 0.1)(4.184) = (151.96 \pm 0.42) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . The value  $S_m^\circ\{(\text{NH}_4)_2\text{HPO}_4, \text{cr}, 298.15 \text{ K}\} = (151.96 \pm 0.45) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  accepted in the CODATA report [13] is identical except for the slightly larger uncertainty. We are not aware of any additional heat capacities for this system and thus accept the value  $S_m^\circ\{(\text{NH}_4)_2\text{HPO}_4, \text{cr}, 298.15 \text{ K}\}$  selected in the CODATA report.

Waterfield and Staveley [34] measured the heat capacities of  $\text{Na}_2\text{HPO}_4\cdot 2\text{H}_2\text{O}(\text{cr})$ ,  $\text{Na}_2\text{HPO}_4\cdot 7\text{H}_2\text{O}(\text{cr})$ , and  $\text{Na}_2\text{HPO}_4\cdot 12\text{H}_2\text{O}(\text{cr})$  from about 5 to 300 K. Only smoothed results were reported. Their derived values are  $S_m^\circ(\text{Na}_2\text{HPO}_4\cdot 2\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (52.90 \pm 0.2)(4.184) = (221.33 \pm 0.84) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ,  $S_m^\circ(\text{Na}_2\text{HPO}_4\cdot 7\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (103.87 \pm 0.3)(4.184) = (434.59 \pm 1.26) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , and  $S_m^\circ(\text{Na}_2\text{HPO}_4\cdot 12\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (148.56 \pm 0.4)(4.184) = (621.58 \pm 1.67) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . Compiled solubilities [35] for the various hydrates of  $\text{Na}_2\text{HPO}_4\cdot x\text{H}_2\text{O}(\text{cr})$  indicate that  $\text{Na}_2\text{HPO}_4\cdot 12\text{H}_2\text{O}(\text{cr})$  is the thermodynamically stable hydrate in contact with the



saturated aqueous solutions below about 308.6 K, and thus this hydrate is the one needed for evaluation of the standard entropy of the  $\text{HPO}_4^{2-}(\text{aq})$  ion.

Waterfield and Staveley [34] also determined the dissociation vapor pressures of the solid mixtures  $\text{Na}_2\text{HPO}_4(\text{cr}) + \text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}(\text{cr})$ ,  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}(\text{cr}) + \text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$ , and  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}(\text{cr}) + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}(\text{cr})$  at 298.15 K, along with the enthalpies of solution of the individual solid phases. Combining this information with  $S_m^\circ(\text{Na}_2\text{HPO}_4, \text{cr}, 298.15 \text{ K})$  from the published literature, they calculated the entropies of the three hydrates. Agreement between calculated and experimental values was good for the two lower hydrates, but the value of  $S_m^\circ(\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (152.07 \pm 0.2)(4.184) = (636.26 \pm 0.84) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  calculated by this method is significantly larger than the value of  $S_m^\circ(\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (621.58 \pm 1.67) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  obtained by integration of the heat capacities, which implies that this solid phase has a large residual entropy of  $14.7 \pm 2.1$  at 0 K due to disorder in the crystal structure. A similar procedure was used in the CODATA evaluation [13], except that the entropy of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}(\text{cr})$  was tied to that of  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$  rather than to  $\text{Na}_2\text{HPO}_4(\text{cr})$ . The resulting CODATA value of  $S_m^\circ(\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (634.6 \pm 1.0) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  is  $1.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  smaller than Waterfield and Staveley's calculated value that was referenced to  $\text{Na}_2\text{HPO}_4(\text{cr})$ .

Because of the uncertainty in the value of  $S_m^\circ(\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K})$  resulting from this residual entropy, it is desirable to also use other thermodynamic cycles to evaluate  $S_m^\circ(\text{HPO}_4^{2-}, \text{aq}, 298.15 \text{ K})$ . Low temperature heat capacities are available for both  $(\text{NH}_4)_2\text{HPO}_4(\text{cr})$  and  $\text{K}_2\text{HPO}_4(\text{cr})$  [36, 37] and, because of the

absence of residual entropies at 0 K, entropies derived from these studies have the potential of yielding a more reliable value of  $S_m^\circ(\text{HPO}_4^{2-}, \text{aq}, 298.15 \text{ K})$ .

Luff *et al.* [36] measured the heat capacities of  $(\text{NH}_4)_2\text{HPO}_4(\text{cr})$  from 8.70 to 316.14 K and derived the value  $S_m^\circ\{(\text{NH}_4)_2\text{HPO}_4, \text{cr}, 298.15 \text{ K}\} = 42.30(4.184) = 177.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . Similarly, Luff and Reed [37] reported heat capacities of  $\text{K}_2\text{HPO}_4(\text{cr})$  from 9.49 to 316.12 K and derived the value  $S_m^\circ(\text{K}_2\text{HPO}_4, \text{cr}, 298.15 \text{ K}) = 42.80(4.184) = 179.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . Assessed values of the standard enthalpies of solution of  $(\text{NH}_4)_2\text{HPO}_4(\text{cr})$  are reported in the CODATA review [13]. Also needed for the evaluation of the standard entropy of solution are the molalities and activity coefficients of the saturated solutions of these electrolytes at 298.15 K. Available compilations [35, 38, 39] indicate that  $m(\text{sat.}) \approx 5.4 \text{ mol}\cdot\text{kg}^{-1}$  for  $(\text{NH}_4)_2\text{HPO}_4$  and  $m(\text{sat.}) \approx 9.5 \text{ mol}\cdot\text{kg}^{-1}$  for  $\text{K}_2\text{HPO}_4$ , both at 298.15 K. Unfortunately, the isopiestic measurements needed to evaluate the activity coefficients do not extend to these high molalities and are available at 298.15 K only from 0.1058 to  $3.107 \text{ mol}\cdot\text{kg}^{-1}$  for  $(\text{NH}_4)_2\text{HPO}_4(\text{aq})$  [40] and from 0.0894 to 0.8861 for  $\text{K}_2\text{HPO}_4(\text{aq})$  [42, 47]. Thus, it is not possible to evaluate the activity coefficients of their saturated solutions and consequently not the standard solubility products of  $(\text{NH}_4)_2\text{HPO}_4(\text{cr})$  and  $\text{K}_2\text{HPO}_4(\text{cr})$ . As a result, the data cited in this paragraph cannot be used to calculate another value of  $S_m^\circ(\text{HPO}_4^{2-}, \text{aq}, 298.15 \text{ K})$ . *We hope that a reader of this paper will perform the needed isopiestic measurement for  $(\text{NH}_4)_2\text{HPO}_4(\text{aq})$  and  $\text{K}_2\text{HPO}_4(\text{aq})$  at 298.15 K from low molalities to saturation because this information would allow two independent checks to be made on the value of  $S_m^\circ(\text{HPO}_4^{2-}, \text{aq}, 298.15 \text{ K})$  derived in*

*the CODATA report and, potentially, improve its value.* More precise solubility determinations are also needed to resolve discrepancies among published values.

The CODATA evaluation derived the standard Gibbs energy of solution of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}(\text{cr})$  at 298.15 K from  $m(\text{sat.}) = 0.812 \text{ mol} \cdot \text{kg}^{-1}$  reported by Wendrow and Kobe [41] and interpolated the isopiestic results of Scatchard and Brekenridge [42] to this molality to yield  $\gamma_{\pm}(\text{sat.}) = 0.223$  and water activity  $a_{\text{w}}(\text{sat.}) = 0.9732$ , which yields the standard solubility product  $K_{\text{s}} = 0.01714$  and  $\Delta_{\text{sol}} G_{\text{m}}^{\circ}(\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -10.080 \pm 0.050 \text{ kJ} \cdot \text{mol}^{-1}$ . However, Wendrow and Kobe cite two other solubility studies at this temperature, and Linke [35] cited those studies along with two additional ones that yield  $m(\text{sat.}) = 0.845$ , 0.855, 0.859, and  $0.828 \text{ mol} \cdot \text{kg}^{-1}$ . These values are all higher than the Wendrow and Kobe solubility, whereas Platford's results [40] yield an agreeing value of  $m(\text{sat.}) = 0.818 \text{ mol} \cdot \text{kg}^{-1}$ . The unweighted mean of these values,  $m(\text{sat.}) = 0.836 \pm 0.039 \text{ mol} \cdot \text{kg}^{-1}$ , agrees within the 95% confidence limits with the CODATA selection. Platford also reported values of  $K_{\text{s}} = 0.016$  from solubility and isopiestic measurements for  $\text{Na}_2\text{HPO}_4(\text{aq})$  solutions and  $K_{\text{s}} = 0.020$  from similar measurements for aqueous  $\text{Na}_2\text{HPO}_4 + (\text{NH}_4)_2\text{HPO}_4$  mixtures, and their average of  $K_{\text{s}} = 0.018 \pm 0.02$  is nearly equal to  $K_{\text{s}} = 0.01714$  obtained in the CODATA review. Therefore, our reexamination of the standard solubility product will not result in a significant change in the entropy of solution of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}(\text{cr})$  and thus the CODATA value of  $S_{\text{m}}^{\circ}(\text{HPO}_4^{2-}, \text{aq}, 298.15 \text{ K}) = -33.5 \pm 1.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  is retained.

The CODATA [13] evaluation reported that they derived the standard Gibbs energy of solution of  $(\text{NH}_4)\text{H}_2\text{PO}_4(\text{cr})$  at 298.15 K from a solubility taken from Linke

[35] along with the estimated value  $\gamma_{\pm}(\text{sat.}) \approx 0.25$ , which gave  $\Delta_{\text{sol}} G_{\text{m}}^{\circ} \{(\text{NH}_4)\text{H}_2\text{PO}_4, \text{cr}, 298.15 \text{ K}\} = 0.57 \pm 0.35 \text{ kJ}\cdot\text{mol}^{-1}$ . Linke actually reported 4 values of the solubility based on a large number of studies that yield  $m(\text{sat.}) = 3.43, 3.62, 3.57$ , and  $3.48 \text{ mol}\cdot\text{kg}^{-1}$ . The CODATA report did not identify which solubility value from Linke was selected, but back-calculation from the Gibbs energy of solution yields  $K_{\text{s}} = 0.7946$  and  $m(\text{sat.}) = 3.566 \text{ mol}\cdot\text{kg}^{-1}$ , which is essentially the third  $m(\text{sat.})$  value from Linke's tabulation [35]. Filippov *et al.* [43] reported  $m(\text{sat.}) = 3.65 \text{ mol}\cdot\text{kg}^{-1}$ , and Egan and Luff [44] reported  $m(\text{sat.}) = 3.62 \text{ mol}\cdot\text{kg}^{-1}$  but did not state if it was a new experimental or literature value. Eysseltová and Dirkse [38] reported  $m(\text{sat.}) = 3.577 \text{ mol}\cdot\text{kg}^{-1}$  from a smoothing of assessed literature data as a function of temperature, which is in reasonable agreement with the CODATA choice.

Filippov *et al.* [43, 45] reported that  $m(\text{sat.}) = 3.65 \text{ mol}\cdot\text{kg}^{-1}$  and  $\ln K_{\text{s}} = -0.62$  at  $298.15 \text{ K}$  based on isopiestic and solubility measurements. These values yield  $K_{\text{s}} = 0.538$  and  $\gamma_{\pm}(\text{sat.}) = 0.201$ ; consequently,  $\Delta_{\text{sol}} G_{\text{m}}^{\circ} \{(\text{NH}_4)\text{H}_2\text{PO}_4, \text{cr}, 298.15 \text{ K}\} = 1.54 \text{ kJ}\cdot\text{mol}^{-1}$ . We believe that this value is more accurate than the value  $0.57 \pm 0.35 \text{ kJ}\cdot\text{mol}^{-1}$  selected in the CODATA evaluation [13] because it is based on an experimental rather than an estimated activity coefficient. Combining this new result with the CODATA value of  $\Delta_{\text{sol}} H_{\text{m}}^{\circ} \{(\text{NH}_4)\text{H}_2\text{PO}_4, \text{cr}, 298.15 \text{ K}\} = 16.20 \pm 0.10 \text{ kJ}\cdot\text{mol}^{-1}$  yields  $\Delta_{\text{sol}} S_{\text{m}}^{\circ} \{(\text{NH}_4)\text{H}_2\text{PO}_4, \text{cr}, 298.15 \text{ K}\} = 49.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . This standard entropy of solution is smaller by  $3.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  than the value implied in the CODATA evaluation, and yields a corresponding reduction in the derived value of  $S_{\text{m}}^{\circ}(\text{H}_2\text{PO}_4^{-}, \text{aq}, 298.15 \text{ K})$  from  $93.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  to  $90.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

The CODATA [13] evaluation also used a separate calculation of  $S_m^\circ(\text{H}_2\text{PO}_4^-, \text{aq}, 298.15 \text{ K})$  based on the standard entropy  $\text{KH}_2\text{PO}_4(\text{cr})$  and its standard Gibbs energies and enthalpies of solution at 298.15 K. They reported that they selected a solubility of  $m(\text{sat.}) = 1.828 \text{ mol}\cdot\text{kg}^{-1}$  and  $\gamma_{\pm}(\text{sat.}) = 0.3306$  from the study of Childs *et al.* [46], which yields  $K_s = 0.3652$  and  $\Delta_{\text{sol}} G_m^\circ(\text{KH}_2\text{PO}_4, \text{cr}, 298.15 \text{ K}) = 2.50 \pm 0.20 \text{ kJ}\cdot\text{mol}^{-1}$  (using the CODATA uncertainty estimate). Childs *et al.* [46] actually reported that  $m(\text{sat.}) = 1.85 \text{ mol}\cdot\text{kg}^{-1}$  rather than  $m(\text{sat.}) = 1.828 \text{ mol}\cdot\text{kg}^{-1}$  as claimed in the CODATA report. Egan and Luff [44] reported a solubility of  $m(\text{sat.}) = 1.78 \text{ mol}\cdot\text{kg}^{-1}$ , but did not state if it was a new experimental or a literature value, Linke [35] cited five literature values and an average value that yields  $m(\text{sat.}) = 1.837 \text{ mol}\cdot\text{kg}^{-1}$ . Makovička<sup>v</sup> and Salomon [39] reported  $m(\text{sat.}) = 1.83 \text{ mol}\cdot\text{kg}^{-1}$  from a smoothing of literature solubilities as a function of temperature, which is essentially in agreement with the CODATA value. Given the concordance of these solubilities, the CODATA choice of  $m(\text{sat.}) = 1.828 \text{ mol}\cdot\text{kg}^{-1}$  is reasonable.

There are four studies reporting isopiestic data for  $\text{KH}_2\text{PO}_4(\text{aq})$  solutions at 298.15 K. Scatchard and Breckenridge's [42] measurements cover the molality range 0.12018 to 1.25414  $\text{mol}\cdot\text{kg}^{-1}$  and Kabiri-Badr and Zafarani-Moattar [47] from 0.1110 to 1.2433  $\text{mol}\cdot\text{kg}^{-1}$ , but these results do not extend close enough to the saturation molality to yield a reliable value of  $\gamma_{\pm}(\text{sat.})$ . The measurements of Stokes [48] extend from 0.0993 to 1.820  $\text{mol}\cdot\text{kg}^{-1}$  (presumably to saturation) and those of Childs *et al.* [46] from 0.8528 to 2.1866  $\text{mol}\cdot\text{kg}^{-1}$  (to oversaturated). Activity coefficients reported in these two studies show some differences, but are nearly indistinguishable near the saturated solution molality, *e.g.*,  $\gamma_{\pm} = 0.332$  [48] and  $\gamma_{\pm} = 0.3328$  [46] at 1.8  $\text{mol}\cdot\text{kg}^{-1}$ .

Given the consistency of the values of  $m(\text{sat.})$  and  $\gamma_{\pm}$  for  $\text{KH}_2\text{PO}_4(\text{aq})$  and their close agreement with the values selected in the CODATA review [13], there is no compelling reason to recalculate the value of  $S_m^\circ(\text{H}_2\text{PO}_4^-, \text{aq}, 298.15 \text{ K}) = 91.3 \pm 1.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  based on data for  $\text{KH}_2\text{PO}_4(\text{aq})$ . However, because of changes for this quantity calculated from data for  $\text{NH}_4\text{H}_2\text{PO}_4(\text{aq})$  as described above, the average value  $S_m^\circ(\text{H}_2\text{PO}_4^-, \text{aq}, 298.15 \text{ K}) = 90.6 \pm 1.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  appears to a better choice than  $92.5 \pm 1.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  recommended in the CODATA review, although the difference is small.

A consistency check can be made using information not considered in the CODATA review [13]. The second acidic dissociation reaction of  $\text{H}_3\text{PO}_4$  can be written as:



Using the revised value of  $S_m^\circ(\text{H}_2\text{PO}_4^-, \text{aq}, 298.15 \text{ K})$ , the entropy change for this dissociation reaction is given by  $\Delta_{\text{dis}} S_m^\circ = S_m^\circ(\text{HPO}_4^{2-}, \text{aq}, 298.15 \text{ K}) + S_m^\circ(\text{H}^+, \text{aq}, 298.15 \text{ K}) - S_m^\circ(\text{H}_2\text{PO}_4^-, \text{aq}, 298.15 \text{ K}) = (-33.5 \pm 1.5) + (0) - (90.6 \pm 1.5) = -124.1 \pm 2.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . Values of this quantity can also be calculated from the temperature dependence of the natural logarithm of the second dissociation constant. Based on their own careful measurements and analysis, Bates and Acree [49] used this approach to obtain  $\Delta_{\text{dis}} S_m^\circ = -123.8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . Similarly, Ender *et al.* [50] obtained  $\Delta_{\text{dis}} S_m^\circ = -29.63 (4.184) = -124.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and Gryzybowski [51]  $\Delta_{\text{dis}} S_m^\circ = -123.8 \pm 0.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , but Gryzybowski also derived a slightly more negative value of  $\Delta_{\text{dis}} S_m^\circ = -126.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  from the older dissociation constant measurements of

Nims [52]. There is very good agreement between these values of  $\Delta_{\text{dis}} S_{\text{m}}^{\circ}$  from the temperature dependence of the logarithm of the second dissociation constant and the value obtained from calorimetry and Gibbs energy of solution measurements. Thus, the recommended values of  $S_{\text{m}}^{\circ}(\text{HPO}_4^{2-}, \text{aq}, 298.15 \text{ K}) = -33.5 \pm 1.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  (CODATA) and  $S_{\text{m}}^{\circ}(\text{H}_2\text{PO}_4^{-}, \text{aq}, 298.15 \text{ K}) = 90.6 \pm 1.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  (revised here) should be fairly reliable.

#### 4. Some effects resulting from inconsistencies between thermodynamic databases

As discussed above and illustrated in Table 1, there are differences and inconsistencies between different thermodynamic databases containing evaluated thermodynamic properties for various compounds and aqueous species of phosphorus. Combining evaluated values for different compounds and aqueous species from different databases without properly accounting for such differences can yield large errors when back-calculating thermodynamic properties for the reactions upon which these evaluations were based. Pandit and Jacob [53] noted that thermodynamic values for the enthalpy and Gibbs energy of formation of  $\text{Mg}_3\text{P}_2\text{O}_8(\text{s})$  had been moved from older databases to some more recent ones without adjusting for the enthalpy difference between red phosphorus (the standard state in earlier tabulations) and white phosphorus ( $\alpha$ -form, the current standard state). Failure to adjust for this difference resulted in errors of 35 to 40  $\text{kJ}\cdot\text{mol}^{-1}$  for values of  $\Delta_{\text{f}}H_{\text{m}}^{\circ}$  and  $\Delta_{\text{f}}G_{\text{m}}^{\circ}$  in some tabulations. This problem may extend to evaluated data for additional compounds and aqueous species as presented in derivative works and presents an additional concern in taking evaluated thermodynamic values from other

than original sources. We note that the thermodynamic properties of the allotropic forms of phosphorus have been recently discussed in detail by Schlesinger [54]. Although white phosphorus is not the thermodynamically stable allotrope, the red and black forms are difficult to prepare in pure form, which makes them less suitable for quantitative thermodynamic measurements.

The difference of  $\Delta(\Delta_f G_m^\circ) = 6.83 \pm 0.06 \text{ kJ}\cdot\text{mol}^{-1}$  found between the Gibbs energies of formation CODATA [13] and NBS [12] evaluations for the protonated and non-protonated orthophosphate ions could yield large errors in solubility predictions if data from these databases or sources derivative to them were combined without properly accounting for differences between the two evaluations. Using hydroxyapatite as an example, if the value of  $\Delta_f G_m^\circ \{\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2, \text{cr}, 298.15 \text{ K}\}$  is taken from the NBS tabulation and  $\Delta_f G_m^\circ \{\text{PO}_4^{3-}, \text{aq}, 298.15 \text{ K}\}$  from the CODATA tabulation, then the calculated solubility product would be in error by a factor of  $(15.7)^6 = 1.51 \times 10^7$  which is very significant. Clearly, values of thermodynamic quantities from different thermodynamic databases should not be used to supplement each other without a careful consideration of consistency among their common members.

Although our assessment of the published databases for orthophosphate species led us to conclude that the CODATA values are probably the best, they are limited to certain “key” compounds and aqueous species at 298.15 K. The Nuclear Energy has been extending the CODATA effort to include many more compounds and aqueous species [14, 21, 55], but these newer evaluations are limited mainly to those of relevance to radioactive waste management. These extensions include the aqueous



“diphosphate” or “pyrophosphate” ions of various degrees of protonation. We recommend strongly that this effort be continued and extended to include many of the natural minerals and additional relevant aqueous species such as the monofluorophosphate ion,  $\text{PO}_3\text{F}^{2-}$ .

## 5. Summary

The combined NBS tables [12] and the CODATA tables [13] of standard thermodynamic properties are widely used in thermodynamic evaluations and geochemical modeling calculations. A comparison of the enthalpies and Gibbs energies of formation reported in these evaluations shows systematic differences of  $\Delta(\Delta_f H_m^\circ) = 6.5 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta(\Delta_f G_m^\circ) = 6.83 \pm 0.06 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively, for  $\text{H}_3\text{PO}_4^0(\text{aq})$ ,  $\text{H}_2\text{PO}_4^-(\text{aq})$ ,  $\text{HPO}_4^{2-}(\text{aq})$ , and  $\text{PO}_4^{3-}(\text{aq})$ . Although the NBS tables do not provide references or information about their evaluation, an examination of the published literature indicated that the NBS values are based on a now-discredited value of the enthalpy of combustion of  $\text{P}(\text{cr})$  from the study of Holmes [28]. We conclude that the thermodynamic values reported in the CODATA tables [13] and the extension of these results by the NEA [14, 21] are more reliable than the NBS values. The CODATA values of the standard enthalpies of formation of the aqueous protonated orthophosphate ions were reported to be based on evaluated values of  $\Delta_f H_m^\circ(\text{P}_4\text{O}_{10}, \text{cr}, 298.15 \text{ K})$  and  $\Delta_f H_m^\circ(\text{PCl}_5, \text{cr}, 298.15 \text{ K})$ . However, an inspection of the source literature led to the conclusion that the CODATA values were probably based only on the  $\text{PCl}_5(\text{cr})$  data and not  $\text{P}_4\text{O}_{10}(\text{cr})$ , although including both sources of data would only result in small differences of about  $0.6 \text{ kJ}\cdot\text{mol}^{-1}$ .

The differences in recommended thermodynamic values for key phosphate species between the NBS/NIST evaluation and the CODATA evaluation have resulted in an unfortunate dichotomy in the development of large thermodynamic databases for geochemical and engineering modeling. Some derivative works are based on NBS/NIST, others on CODATA. Worse still, data in some cases may have a mixed pedigree (and therefore are inconsistent) or even be of uncertain origin. A further hazard in developing large thermodynamic databases including phosphorus is that some evaluated data in existing popular compilations may not have been corrected from the older red phosphorus reference state to the currently accepted one based on white phosphorus. For all of these reasons, in developing the phosphate part of large databases for thermodynamic modeling, the use of existing popular compilations in place of original sources carries risk that has perhaps not been fully appreciated.

The calculations of the standard entropies of the  $\text{H}_2\text{PO}_4^-$ (aq) and  $\text{HPO}_4^{2-}$ (aq) ions were reexamined in light of more recently published thermodynamic data and data not considered in the CODATA review. We note that if experimental isopiestic measurements at 298.15 K for  $(\text{NH}_4)_2\text{HPO}_4$ (aq) and  $\text{K}_2\text{HPO}_4$ (aq) extending to saturation and more precise solubility determinations become available, then they could be combined with available standard entropies of the solid phases to yield two additional values of  $S_m^\circ(\text{HPO}_4^{2-}, \text{aq}, 298.15 \text{ K})$ . These new values would allow the reliability of the value reported in the CODATA review to be checked and improved. Our analysis of literature data suggests that  $S_m^\circ(\text{H}_2\text{PO}_4^-, \text{aq}, 298.15 \text{ K}) = 90.6 \pm 1.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  is a better choice than  $92.5 \pm 1.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  recommended in the CODATA review, although the difference is small. A comparison of entropy of

dissociation of  $\text{H}_2\text{PO}_4^-(\text{aq})$  to form  $\text{HPO}_4^{2-}(\text{aq})$  calculated using a CODATA-type thermodynamic cycle, with that obtained from the temperature dependence of the dissociation constant, shows very good agreement.

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**Table 1** Comparison of published values of the standard molar enthalpies of formation,  $\Delta_f H_m^\circ$ , standard molar Gibbs energies of formation,  $\Delta_f G_m^\circ$ , and standard molar entropies,  $S_m^\circ$ , of  $\text{PO}_4^{3-}(\text{aq})$ ,  $\text{HPO}_4^{2-}(\text{aq})$ ,  $\text{H}_2\text{PO}_4^-(\text{aq})$ ,  $\text{H}_3\text{PO}_4^0(\text{aq})$ ,  $\text{P}(\text{cr, white})$ ,  $\text{P}_4\text{O}_{10}(\text{cr})$  and  $\text{PCl}_5(\text{cr})$  at 298.15 K (25 °C)

Compound or ion	Selected Values (1952) <sup>a</sup>	NBS 270-3 (1968) <sup>b</sup>	NBS Tables (1982) <sup>c</sup>	CODATA (1989) + NEA (1992) <sup>d</sup>	Gurvich <i>et al.</i> (1989) <sup>e</sup>	NIST-JANAF (1998) <sup>f</sup>
$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )						
$\text{H}_3\text{PO}_4^0(\text{aq})$		-1288.3	-1288.34	-1294.12		
$\text{H}_2\text{PO}_4^-(\text{aq})$	-1302.5	-1296.3	-1296.29	-1302.6		
$\text{HPO}_4^{2-}(\text{aq})$	-1298.7	-1292.1	-1292.14	-1299.0		
$\text{PO}_4^{3-}(\text{aq})$	-1284.1	-1277.4	-1277.4	-1284.4		
$\text{P}_4\text{O}_{10}(\text{cr,hex})$	-3012.5	-2984.0	-2984.0	(-3008.2) <sup>g</sup>	-3010.1	-3009.9
$\text{PCl}_5(\text{cr})$	-463.2	-443.5	-443.5	(-443.85) <sup>h</sup>		
$\text{P}(\text{cr, white})$	0	0	0	0	0	0
$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )						
$\text{H}_3\text{PO}_4^0(\text{aq})$		-1142.65	-1142.54	-1149.367		
$\text{H}_2\text{PO}_4^-(\text{aq})$	-1135.1	-1088.6 <sup>i</sup>	-1130.28	-1137.152		
$\text{HPO}_4^{2-}(\text{aq})$	-1094.1	-1089.3	-1089.15	-1095.985		
$\text{PO}_4^{3-}(\text{aq})$	-1025.5	-1018.8	-1018.7	-1025.491		
$\text{P}_4\text{O}_{10}(\text{cr,hex})$		-2697.8	-2697.7			-2723.3
$\text{PCl}_5(\text{cr})$						
$\text{P}(\text{cr, white})$	0	0	0	0	0	0
$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )						
$\text{H}_3\text{PO}_4^0(\text{aq})$		158.2	158.2	161.912		
$\text{H}_2\text{PO}_4^-(\text{aq})$	89.1	90.4	90.4	92.5		
$\text{HPO}_4^{2-}(\text{aq})$	-36.0	-33.5	-33.5	-33.5		
$\text{PO}_4^{3-}(\text{aq})$	-218	-222	-220.3 <sup>j</sup>	-220.97		
$\text{P}_4\text{O}_{10}(\text{cr,hex})$		228.9	228.86		231.00	228.78
$\text{PCl}_5(\text{cr})$						

P(cr, white)	44.35	41.09	41.09	41.09	41.09	41.08
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<sup>a</sup> From Rossini *et al.*, “Selected Values of Chemical Thermodynamic Properties” [10].

Units of calories were converted to joules using  $1 \text{ cal}_{\text{th}} = 4.1840 \text{ J}$ .

<sup>b</sup> From Wagman *et al.*, Technical Note 270-3 [11]; values taken with possibly minor corrections from either Technical Note 270-1 or 270-2. Units of calories were converted to joules using  $1 \text{ cal}_{\text{th}} = 4.1840 \text{ J}$ .

<sup>c</sup> From Wagman *et al.*, “The NBS tables of chemical thermodynamic properties” [12].

<sup>d</sup> From Cox *et al.*, “CODATA Key Values for Thermodynamics” [13], and Grenthe *et al.*, “Chemical Thermodynamics of Uranium” [14]. The CODATA Key Values of 1989 [13] were accepted by Grenthe *et al.* and supplemented with calculations of  $\Delta_f G_m^\circ$ , along with some additional evaluations.

<sup>e</sup> From Gurvich *et al.*, “Thermodynamic Properties of Individual Substances” [18].

<sup>f</sup> From Chase, “NIST-JANAF Thermochemical Tables” [19]. The values given by Barin in “Thermodynamic Data for Pure Substances” [20] for  $\text{P}_2\text{O}_{10}(\text{cr})$  and  $\text{P}_2\text{O}_{10}(\text{g})$  are essential identical to the NIST-JANAF values.

<sup>g</sup> This value was not given in the CODATA Key Values but was involved in thermodynamic cycles to obtain  $\Delta_f H_m^\circ$  of the various hydrogen phosphate ions. This value was derived in this report; see the discussion in the text.

<sup>h</sup> This value was not given in the CODATA Key Values but was used in thermodynamic cycles to obtain  $\Delta_f H_m^\circ$  of the various hydrogen phosphate ions; it was taken from Schumm *et al.* [16].

<sup>i</sup> This value of  $\Delta_f G_m^\circ$  is apparently erroneous because  $\Delta_f G_m^\circ = -1130.3 \text{ kJ}\cdot\text{mol}^{-1}$  is obtained using their reported values of  $\Delta_f H_m^\circ$  and  $S_m^\circ$ ; this derived value agrees with that reported in the NBS Tables of Chemical Thermodynamic Properties [12].

<sup>j</sup> This value was reported in the errata for the NBS Tables of Chemical Thermodynamic Properties [12].